Solvothermal deposition and characterization of magnesium hydroxide nanostructures on zeolite crystals

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Abstract

A methodology to engineer roughened inorganic nanostructures on zeolites by deposition and growth of metal hydroxides is reported. Pure-silica (PS) MFI and (aluminosilicate) LTA zeolite crystals are treated by solvothermal methods to deposit inorganic hydroxide (e.g., Mg(OH)2) coatings with nanoscale roughened features on the crystal surfaces in a controlled manner. Detailed characterization of the surface-modified MFI crystals by nitrogen physisorption allows the quantification of the surface roughness of the Mg(OH)2 nanostructures. Pore volume characterization shows that solvothermal deposition has only a marginal effect on the porosity of the MFI. The surface-roughened zeolites are used to fabricate zeolite/polymer mixed matrix films with considerably improved interfacial adhesion properties. Solvothermal deposition of inorganic nanostructures is also demonstrated on zeolite LTA crystals, which present aluminosilicate surfaces. In this case, the intracrystalline sodium ions in LTA are partially substituted with magnesium ions from the reagent solution during treatment. The solvothermal treatment is thus modified to deposit smaller Mg(OH)2 nanostructures, resulting in more roughened zeolite LTA surfaces. Our detailed characterization reveals that the surface-treated LTA crystals may be promising materials for applications in mixed matrix membranes.

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1. Introduction

The fabrication of composite films and membranes is often an effective way to combine the advantages of two disparate materials and to minimize their drawbacks. For example, there has been increasing interest in composite membranes for a variety of chemical separation applications [1–4]. Membrane-based gas separation offers several advantages including ease of operation, lower energy requirements and lower operating costs over conventional gas separation processes [4]. Polymeric membranes have been utilized in commercial applications [5], and their mechanical properties and processability are attractive. However, existing polymeric membrane materials are limited by an inherent trade-off: an improvement in permeability is accompanied by a loss of selectivity, or vice versa [6,7]. Meanwhile, high-performance inorganic molecular sieve membranes have been developed using zeolites and other materials [8,9]. The accurate size and shape discrimination originating from the uniform nanopores in molecular sieve materials ensures superior selectivity. However, the cost of processing these inorganic membranes is significantly higher than that of polymeric membranes [8].

One promising way to achieve high separation performance is to incorporate molecular sieves into polymer membranes [4]. In this “mixed matrix membrane” concept, one can combine the easy processability and good mechanical properties of the polymer with the high separation performance of the molecular sieve. Many studies have demonstrated the high separation performance of mixed matrix membranes exhibiting performance beyond the intrinsic properties of polymers [4,10–12]. However, problems have been associated with the presence of poor interfacial morphologies between the inorganic fillers and polymers. Many researchers have demonstrated that adhesion problems occur at the polymer/zeolite interface [4]. The poor polymer/zeolite adhesion results in interfacial voids that are often visible in SEM images, and which are the major cause for deterioration in separation performance. Diffusing molecules take a non-selective and low-resistance path through the voids, bypassing the embedded molecular sieve.

Various methods for surface functionalization of zeolites have been investigated. Silane chemistry is one of the most well-studied methods to functionalize the surface of zeolites or silica for fabrication of composite materials. In general, the silane coupling agents used have two functional moieties: reactive surface groups such as alkoxides at one end, and a functional group intended to interact with the polymer at the other end. The coupling agents are anchored on the zeolite surface by condensation reactions...
between the silanol groups on the zeolite surface and the alkoxides in the silane reagent. By covalent (or other) bonding of the pendant functional group at the other end of the coupling agent with functional groups in polymer chains, the coupling process between inorganic fillers and polymers is accomplished. For example, silane coupling agents with amine functionalities can be used to fabricate mixed matrix membranes with poly(imide)s, since the pendant amine group can react with imide rings in the polymer to form covalent bonds [13]. In other studies, poly(imide)s with carboxylic acid groups were synthesized to generate chemical bonding with amine groups in silane coupling agents [14]. Adhesion between the zeolite and polymer can also be enhanced without chemical bonding between the coupling agent and polymer, for example by van der Waals or hydrogen bonding interactions [15,16]. However, Husain et al. reported that there can be non-selective gas permeation through gaps between the zeolite and polymer due to insufficient organic loading [15]. Similarly, enhancement of gas separation performance of mixed matrix membranes made with zeolite A and poly(sulfone) was not satisfactory when a silane coupling agent with amine functionality was used [16]. Consequently, methods other than silane chemistry may be desirable for polymer/inorganic sieve compatibilization.

Shu et al. reported that a "nano-whisker structure" could be created on the surface of zeolite A via a halide/Grignard route [11,17]. Highly roughened surfaces created by formation of Mg(OH)2 nano-crystals on the zeolite surface provided enhanced interactions at the polymer/particle interface, via possible adsorption and interlocking of polymer chains in the whisker structure. The resultant mixed matrix membrane demonstrated significant improvement in gas separation performance. However, this method utilizes a complicated procedure and highly unstable reactants, and may not be cost effective. Thus, the development of rational methods to create such nanostructures, using more benign chemistry that is amenable to scale-up, would be highly attractive. Mg(OH)2 crystals can be formed by reactions between a magnesium source, a base and water. There are several studies that demonstrate the formation of Mg(OH)2 nanostructures via precipitation at moderate temperatures [18–21] or hydrothermal processes [22–25]. The type and concentration of both the magnesium source and base [18,19], reaction time [25], pH (in aqueous processes) [18,19,23] and reaction temperature [23] are important factors affecting crystallinity and morphology of resulting nanomaterials. It was reported that nano-needles or nano-rods could be obtained by the addition of a dispersant such as polyethylene glycol [21], surfactants and solubility of proteins [20]. In these methods, Mg(OH)2 crystals were formed rapidly via homogeneous precipitation. Meanwhile, it was also shown that well-defined Mg(OH)2 nanorods could be created solvothermally with a non-aqueous solvent [25,26]. In this method, ethylenediamine acted as both reaction medium and base. Magnesium sources and a small amount of water were the other components of the reaction mixture. It was found that both the nature of the magnesium source and the ethylenediamine/water ratio were key factors affecting the resultant crystal morphology. For instance, nanorods could be formed from magnesium powder and MgSO4, but only platelets were obtained using Mg(NO3)2 as the metal source. A high ethylenediamine-to-water ratio was also essential to create nanoneedles or nanorods. Although the true role of ethylenediamine is unclear, the authors speculated that the selective interaction between the coordinating solvent (ethylenediamine) and surface ions (Mg2+) slows the growth of specific lattice planes, resulting in one dimensional growth of nanocrystals.

To create nanostructured morphologies on zeolite surfaces based on the aforementioned methods, the synthesis conditions should be modified to allow the precipitation of inorganic crystals on the zeolite surface in a controlled manner, rather than precipitation in the solution independent of the zeolite surfaces. Thus, heterogeneous deposition, as well as heterogeneous nucleation and growth on the zeolite surface, are both desirable effects. Very recently, we reported a facile solvothermal method to deposit inorganic nanostructures on PS–MFI surfaces [27]. Enhanced gas separation performance was achieved with mixed matrix membranes containing surface modified PS–MFI due to improved polymer/zeolite adhesion. Specifically, mixed matrix membranes prepared by dispersing the functionalized zeolite in Ultem® and Matrimid® polymers showed dramatic increases in CO2 throughput while maintaining high selectivity over CH4. Furthermore, O2 and N2 permeation data elucidated the role of interface quality in determining the membrane properties. Here we report a detailed study of solvothermal methods to grow inorganic nanostructures on the surface of zeolites. Two zeolites with different surfaces, aluminosilicate zeolite LTA and PS–MFI, were used as model substrates. We demonstrate the tuning of the solvothermal surface modification chemistry to deposit a range of fine nanostructures, resulting in highly roughened zeolite surfaces. The structural properties of these modified zeolites relevant to their application in composite films are thoroughly investigated.

2. Experimental section

2.1. Materials

The following chemicals were commercially available and were used as received: tetraethylorthosilicate (TEOS, 98% Sigma–Aldrich), tetrapropylammonium hydroxide (TPAOH, 40% w/w aqueous solution, Alfa Aesar), tetrapropylammonium bromide (TPABr, 98%, Sigma–Aldrich), tetrathylammonium hydroxide (TMAOH, 25% in water, Sigma–Aldrich), ethylenediamine (EDA, 99%, Sigma–Aldrich), diethylenetriamine (DETA, 99%, Sigma–Aldrich), methylmagnesium bromide (3 M in ether, Sigma–Aldrich), 2-propanol (Sigma–Aldrich), dichloromethane (DCM, 99.5%, Sigma–Aldrich), toluene (99.8%, Sigma–Aldrich), colloidal silica (Ludox HS-30, Sigma–Aldrich), and aluminum isopropoxide (Al(OiPr)3, 97%, Sigma–Aldrich), magnesium sulfate heptahydrate (Acros) and sodium chloride (Fisher Scientific).

2.2. Synthesis of zeolite MFI

Pure-silica MFI crystals were synthesized hydrothermally at 150 °C from TEOS/TPAOH/water solutions. The TEOS/TPAOH molar ratio was 1:0.36 or 1:0.24 and the water content was varied from 20 to 360 on a molar basis as part of a synthesis matrix that included variation in the reaction time (2–4 days). The general methodology otherwise followed that described in our previous work [28]. Large crystal MFI was also prepared using the method described in the literature [29]. The solution with molar ratio of 1TEOS:0.1TPABr:0.1NaOH:98H2O was aged at 50 °C for 7 days and crystallized at 120 °C for 2 days. The zeolite particles were repeatedly centrifuged and washed with deionized water at least 5 times, and dried at 80 °C. Finally, calcination was performed at 550 °C for 8 h in air to remove the structure-directing agent from the zeolite pores.

2.3. Synthesis of zeolite LTA

LTA particles were synthesized hydrothermally based on the method published by Larlus et al. [30]. Colloidal silica (Ludox HS-30) and aluminum isopropoxide were used as silicon and aluminum sources, respectively and the structure directing agent was TMAOH. For 300 nm particle synthesis, clear precursor solution with molar ratio of 0.2NaOH:1SiO2:1Al(OiPr)3:4TMAOH:17H2O was prepared at room temperature and treated hydrothermally at
60 °C for 1 day, and at 100 °C for 1 day, correspondingly. Large crystal LTA, approximately 1–2 μm, was also prepared from the solution with molar ratio of 0.2NaOH: 1SiO₂: 1Al(OiPr)₃: 2.4TMAOH:250H₂O. The hydrothermal reaction was conducted at 120 °C for 4 days. The zeolite particles were repeatedly centrifuged and washed with deionized water at least 5 times, and dried at 80 °C. Finally, calcination was performed at 550 °C for 8 h in air.

2.4. Grignard treatment

After dispersing 0.5 g of zeolite in 3 M aqueous NaCl solution, the suspension was filtered using a microfiltration membrane with 0.1 μm pores to collect the particles. To remove some of the residual water, the particles were dried at 80 °C overnight. The NaCl seeded particles were placed in round bottom flask and 8 ml of toluene was added. After purging the flask with nitrogen, 1.5 ml of 3 M CH₃MgBr in ether was added using a transfer needle. The suspension was sonicated for 4 h and then stirred for 12 h at room temperature under nitrogen. 2-propanol was added drop-wise to quench the Grignard reagent and the mixture was centrifuged to collect the particles. To remove residual solvents, the particles were washed with 2-propanol several times. Then, 40 ml of deionized water was added and the mixture was sonicated for 2 h. During the sonication, the temperature increased to 43–45 °C. The particles were repeatedly centrifuged and washed with deionized water (at least 5 times), and dried at 80 °C.

2.5. Solvothermal treatment

After dispersing 0.2 g of zeolites in 10 ml of ethylenediamine (EDA) by sonication, 1 ml of 1 M aqueous MgSO₄ solution was added dropwise to the dispersion while applying vigorous stirring. After further stirring for 1 h, the mixture was transferred to a Teflon-lined autoclave and solvothermal treatment was performed at 160 °C for 12 h. The particles were washed with deionized water by several repetitions of sonication and centrifugation and dried at 80 °C. Zeolite LTA was also treated with diethylenetriamine (DETA) as an organic base. In this method, MgSO₄ powder was used as a magnesium source. After dispersing 0.2 g LTA in 10 ml DETA placed in 23 ml volume Teflon cup, 1 mmol of MgSO₄ powder was added. The mixture was further sonicated for 1 min using a sonication horn and transferred to an autoclave reactor after adding 1 ml of deionized water. The solvothermal reaction was conducted at 180 °C for 12 h, and the particles were then washed with deionized water by several cycles of sonication and centrifugation. To remove residual DETA from zeolites, more intense washing was often needed. For example, surface treated LTA crystals were further washed by stirring in water at 80 °C for 1 day.

2.6. Mixed-matrix composite film fabrication

Zeolite/polymer composite films were prepared using a solution casting technique. Zeolite particles were dispersed in DCM using a sonication horn. Poly(etherimide) (Ultem™ 1000) was added to the suspension, which was then stirred overnight. After pouring the solution on a glass plate, a nascent film was cast using a “doctor’s knife”. Finally, a dense film was obtained after drying at room temperature.

2.7. Characterization

The morphologies of both zeolite particles and composite films were observed with a scanning electron microscope (SEM, LEO 1530). In order to observe the true morphology of the roughened surfaces, the zeolite particles were imaged without previously sputtering a gold layer on to the sample. On the other hand, the mixed matrix membrane samples were sputtered with gold after being cryogenically fractured in liquid nitrogen. Energy dispersive X-ray spectroscopy (EDS) was used to investigate the elemental composi-

Fig. 1. SEM images of PS–MFI particles; (a) 5 μm large crystal; (b)–(c) crystals synthesized from the precursor solution composition of 1 TEOS: x TPAOH: y H₂O for z days. (b) 2 μm, x = 0.24, y = 360 and z = 4; (c) 300 nm, x = 0.36, y = 180 and z = 2; (d) 100 nm, x = 0.36, y = 20 and z = 4.
tion of the zeolites. Bulk compositions were also measured with ICP–AES (inductively coupled plasma atomic emission spectroscopy) with an outside vendor, Columbia Analytical Services Inc. Micropore volume (by the t-plot method) and Brunauer–Emmett–Teller (BET) surface area were calculated from nitrogen physisorption measurements performed on an ASAP 2020 or 2010 (Micromeritics). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a Netzsch STA409. Samples were heated under a nitrogen-diluted air stream from 30 to 900 °C at a rate of 10 °C/min. Powder X-ray diffraction (XRD) patterns were obtained on a PANalytical X’pert diffractometer operating with Cu Kα radiation and equipped with an X’celerator detector.

3. Results and discussion

3.1. Solvothermal treatment of PS–MFI zeolite

3.1.1. Zeolite MFI synthesis and characterization

Examples of the MFI particles synthesized for this study are shown in Fig. 1. The largest crystals were made using TPABr as a
structure-directing agent (SDA) and were approximately 5 μm in size (Fig. 1a). The particles showed a broad size distribution. In contrast, crystals synthesized with TPAOH as the SDA showed uniform sizes. Crystals of 100 nm, 300 nm and 2 μm size were synthesized by adjusting the reaction time, and the amount of SDA or water. As the particle size increased, the morphology of the particles changed from spherical (100 nm) to prismatic (2 and 5 μm). As shown in Fig. S1, all the synthesized crystals exhibited typical XRD patterns of MFI.

3.1.2. Morphology of surface treated PS–MFI

Fig. 2 shows the morphology of MFI particles surface-treated with both solvothermal and Grignard routes. Roughened surfaces were created by the formation Mg(OH)2 nanostructures on the surface of MFI. As shown in the Fig. 2a and c, the solvothermal treatments created well-defined whisker structures on the surface of prismatic 5 μm and 2 μm crystals, since the particles provide a large planar surface for the inorganic nanostructures to be immobilized. However, the morphology of 300 nm MFI particles was changed to a “cotton-ball” structure, as the size of particles became closer to the size of the nanostructures created. This phenomenon was also reported in the Grignard treatment by Shu et al. [17]. Meanwhile, for 100 nm MFI crystals, the surfaces were coated with very fine structures without a distinguishable whisker-like morphology. Furthermore, particle aggregation was significant when compared to other larger MFI particles, as shown in Fig. 2g. In contrast, Grignard treatment created nanowhisker structures on the zeolite surfaces as well as inorganic platelet structures in solution. The amount of surface nanostructures created was smaller than that in solvothermally treated MFI, as seen initially by visual comparison.

3.1.3. Mass fraction of Mg(OH)2

The bulk compositions of surface-treated MFI particles were measured by ICP–AES. From the Si and Mg contents, the mass fraction of Mg(OH)2 was calculated after assuming the samples are comprised only of SiO2 and Mg(OH)2. The mass fraction of Mg(OH)2 could also be estimated by TGA. A sharp endothermic peak in the range of 370–430 °C appears in the DSC curve (Fig. 3) due to the dehydration of Mg(OH)2 to MgO. The mass of Mg(OH)2 was calculated from the H2O loss in this temperature region, and the results are summarized in Table 1. In general, results from both types of measurements showed good agreement. The mass fraction of Mg(OH)2 in Grignard treated PS–MFI increased as the particle size decreased, since the smaller particles provide larger surface area per unit mass. However, in contrast to Grignard treatment, there was no relationship between the amount of Mg(OH)2 and the MFI particle size in solvothermally treated MFI crystals, since the reaction continued until all the magnesium source in the reactant solution was consumed. The yield from the solvothermal reaction was so high that the mass fractions of Mg(OH)2 were close to the theoretical maximum for all batches of particles.

3.1.4. Surface roughness

Visual observation of SEM photographs indicates a high surface roughness of the nanostructures created by solvothermal treatment. However, the surface roughness can be quantified, since it is strongly related to the external surface area. We measured the BET surface area after surface treatment on uncalcined MFI particles (whose internal micropores are blocked because of the presence of the SDA in them). In this study, 300 nm and 2 μm MFI crystals were chosen as representative samples, and the surface areas obtained from nitrogen physisorption measurements were normalized by the masses of zeolite and Mg(OH)2 (which are obtained from ICP–AES measurements). Table 2 shows the BET surface area of bare and surface-treated uncalcined MFI particles. For both 300 nm and 2 μm MFI, surface roughness increased significantly after surface treatment. In addition, solvothermally treated MFI particles showed higher surface areas than Grignard treated samples, consistent with SEM observations. Normalization with the mass of Mg(OH)2 showed that finer nanostructures were formed on 300 nm crystals in comparison to the 2 μm MFI crystals, via both the surface treatment methods. On the surface of 2 μm MFI crystals, the size of Mg(OH)2 nanostructures created by both treatments were quite similar. However, for 300 nm particles, the nanostructures from the solvothermal treatment were smaller than those from the Grignard treatment.

3.1.5. Powder X-ray diffraction

Powder XRD patterns of solvothermally surface-treated PS–MFI were measured. As shown in Fig. 4a, all particles maintain the MFI structure after the solvothermal treatment. Even though the treatment was performed in a basic environment at 160 °C, the MFI framework is observed to be robust. It was initially expected that peaks from Mg(OH)2 could be detected by powder XRD measurements. However, there were no distinguishable peaks from Mg(OH)2 except a broad peak at 38° 20. XRD patterns of MFI
particles treated with Grignard reagent are also shown in Fig. 4b. All particles also maintained the MFI framework structure after the treatment. For large crystals such as 5 and 2 µm particles, only peaks from MFI were observed due to the high crystallinity of the zeolite. However, as the particle size decreased to 100 nm, the relative contribution of diffraction from the surface nanostructures became distinguishable, and the positions of these new XRD peaks matched those of crystalline Mg(OH)$_2$ (brucite) [19,20,24]. Hence, we conclude that nanostructures obtained by Grignard treatment are more crystalline whereas those obtained by solvothermal treatment are likely X-ray amorphous (i.e., either composed of very small crystalline domains, or entirely amorphous). At present, there is no indication of the respective advantages of amorphous versus crystalline surface nanostructures.

3.1.6. Micropore volume of surface-treated MFI

It is possible that species involved in the surface nanostructure formation can plug (block) the micropores of MFI, resulting in substantial pore volume reduction. If the nanostructure deposition is accompanied by a significant loss of microporosity, use of the surface treatments can further reduce the available pore volume. The isotherms in Fig. 5 show an apparent decrease in the micropore volume capacity of 100 nm MFI in the low pressure region. The pore volume reduction was caused by the use of the surface treatments. For 100 nm particles, the pore volume decreased from 0.15 (bare MFI) to 0.08 (0.13) cm$^3$/g zeolite by solvothermal (Grignard) treatment, respectively. The pore volume reduction was negligible for larger crystals.

![Fig. 4. XRD patterns of surface treated PS–MFI particles; (a) solvothermal treatment and (b) Grignard treatment. Peaks denoted by arrows are due to crystalline Mg(OH)$_2$.](image)

![Fig. 5. Nitrogen physisorption isotherm of PS–MFI particles, 300 nm (top) and 100 nm (bottom).](image)

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Micropore volume of untreated and surface treated PS–MFI.</th>
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<td></td>
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<td></td>
<td>cm$^3$/g sample</td>
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<td>Solvothermal</td>
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<td>Grignard</td>
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3.1.7. Mixed matrix composite films

To investigate the compatibility of the surface-treated MFI particles with polymers, mixed matrix films were prepared using Ultem® and 300 nm MFI as the two components. Fig. 6 shows SEM images of the cross-sections of Ultem®/untreated (bare) MFI and Ultem®/solvothermal–MFI membranes. Voids at the interface are clearly seen in composite membranes fabricated with bare MFI. These “sieve-in-a-cage” morphologies have been reported in many previous studies [11,13,15,31]. Furthermore, the particles formed clusters in the polymer matrix, resulting in a non-uniform distribution. On the other hand, the film morphology was substantially improved by the use of MFI with nanostructured surfaces. Mixed matrix membranes fabricated with solvothermally treated MFI showed practically no interfacial voids by visual observation of the SEM images. Furthermore, all particles were uniformly distributed in polymer matrix, in contrast to the membrane prepared with bare MFI - a further indication of favorable interfacial adhesion between the molecular sieve and polymer. We have previously shown [27] that such a membrane morphology is strongly correlated to favorable separation characteristics.

3.2. Zeolite LTA synthesis and characterization

3.2.1. Synthesis of LTA

The gas separation performance of zeolite LTA, possessing 0.41 nm micropores, is well matched with that of glassy polymers; hence it has been used in a substantial amount of work on mixed matrix membranes for (the industrially very important) O₂/N₂ and CO₂/CH₄ separations. Therefore, we have also studied the surface treatment of zeolite LTA as another important model zeolite. The results of hydrothermal synthesis of LTA are shown in the SEM images of the as-synthesized particles in Fig. 7a and b. Well-defined cubic shape crystals with ~300 nm and ~1.5 μm average sizes were prepared. The zeolite LTA crystals have broader size distributions than the MFI crystals discussed above. Fig S2 shows powder XRD patterns of the LTA crystals.

3.2.2. Morphology and powder X-ray diffraction

As in the case of MFI, solvothermal treatment using ethylenediamine (EDA) as an organic base was performed on LTA crystals (referred as Solvo-EDA). For 1–2 μm crystals, 0.5 M MgSO₄ was used so the amount of magnesium would be half of that used for treatment of 300 nm crystals. As shown in Fig. 7c and d, the smooth surfaces of zeolite LTA became highly roughened by the Mg(OH)₂ whiskers, so that the particles look like “cotton balls”. Powder XRD measurements revealed that the LTA structure was retained after treatment (Fig. S3). A weak and broad reflection at 18°, as well as a stronger peak at 38°, were observed, presumably due to Mg(OH)₂ nanorods. Our study indicates that solvothermal treatment with EDA may allow a general method to create inorganic nanostructures on various oxide surfaces such as pure silica and aluminosilicate surfaces. In a previous study, Mg(OH)₂ nanorods or nanoneedles were solvothermally synthesized in EDA/water mixtures, and the authors have proposed that the controlled growth of Mg(OH)₂ nanorods originates from the formation of complexes of Mg²⁺ and two EDA ligands followed by their linear alignment and condensation [25,26]. Also they found that a high EDA/water ratio was essential for the formation of nanorods or “nanoneedles”. In this study, we also used a high EDA/water volumetric ratio (~10). Control experiments revealed that low EDA/water ratios caused homogeneous precipitation of Mg(OH)₂ and poor quality surface functionalization. For example, an EDA/water ratio of 1 resulted in thin, flat layers of Mg(OH)₂ on 2 μm MFI surfaces, whereas 1–2 μm LTA crystals were hardly functionalized (Fig. S4).

Solvothermal treatment was also performed with DETA as an organic base (referred as Solvo-DETA). This variation was based upon the hypothesis that DETA complexes the magnesium ion more strongly, thus leading to the formation of a larger number of Mg-DETA nuclei that transform into Mg(OH)₂ “nanowhiskers”. The powder form of MgSO₄ was directly used in this treatment instead of an aqueous solution. For 1–2 μm LTA crystals, 0.5 mmol of MgSO₄ powder (half of the amount used for 300 nm LTA) was added to 0.2 g LTA. As shown in Fig. 7e and f, the surface treatment
was successful and the resulting LTA crystals had a “cotton-ball” appearance due to the formation of Mg(OH)₂ nanowhiskers on the surfaces. The powder XRD pattern of this material was similar to that of LTA crystals treated with EDA (Fig. S3).

3.2.3. Thermogravimetric analysis, nitrogen physisorption, and elemental analysis

The Mg(OH)₂ mass fraction in surface treated 300 nm LTA crystals was estimated by TGA (Table 4). The reaction yield was very high and the mass fraction was close to the stoichiometric maximum for solvothermal treatments using either EDA or DETA. However, since even the uncalcined zeolite LTA has some microporosity unlike uncalcined MFI (Fig. S5), the method used for MFI could not be applied directly. Instead, we used the BET external surface area calculated by a t-plot of the data from the nitrogen physisorption measurement on calcined LTA to estimate the external surface area. Fig. 8 shows nitrogen physisorption isotherms of 300 nm untreated (bare) and treated zeolite LTA crystals. The corresponding BET external surface areas are summarized in Table 4. All numbers were normalized by masses of zeolite and Mg(OH)₂, respectively. It is clear that surface roughness of zeolite LTA dramatically increased after deposition of Mg(OH)₂ whisker structures. As hypothesized earlier, the solvothermal treatment with DETA gave rise to higher surface area per unit mass of Mg(OH)₂ than by the EDA route, indicating that smaller/finer nanostructures were created using DETA. Furthermore, it is advantageous to use the milder reaction conditions of the DETA route. The reaction temperature is lower than the boiling point of the solvent (hence reducing the vapor pressure in the reactor). DETA is also a larger molecule than EDA, and does not access the pores of the zeolite as easily as EDA. This enables easier evacuation of the solvent and activation of the micropore volume.

Elemental compositions of both untreated and treated LTA were measured (Table 5) by EDS. After the surface treatment, the Na/Al
ratio dramatically decreased, presumably due to ion exchange of extraframework intracrystalline Na\(^+\) in LTA with Mg\(^{2+}\) from the reactant solution. This hypothesis is further supported by nitrogen physisorption measurements. Unlike the case of MFI, surface treatments gave rise to substantial micropore volume changes in LTA. As shown in Table 4, solvothermally treated LTA showed higher micropore volume than the original Na-LTA. A control experiment revealed that ion-exchanged Mg-LTA has a higher pore volume than Na-LTA. Since two Na\(^+\) ions are replaced by a Mg\(^{2+}\) ion, the micropore volume increased from 0.17 to 0.24 cm\(^3\)/g (Fig. 8a). Micropore volumes of surface-treated LTA crystals were 2.1 and 2.0 cm\(^3\)/g SiO\(_2\), by the EDA and DETA routes, respectively. These values are intermediate between those of Na-LTA and Mg-LTA, indicating a partial ion exchange of Na\(^+\) with Mg\(^{2+}\). Thus, the molecular sieving/transport properties of LTA could be altered because it is well known that the effective size of the micropores in LTA can be varied by ion-exchange. For example, Ca-LTA ("5A") has 0.5 nm pore size in contrast to 0.41 nm for Na-LTA ("4A"). This issue can be addressed in our forthcoming publications, but is beyond the scope of this report. The EDS measurements (spuriously) indicate a higher magnesium content than the stoichiometric maximum, since the technique emphasizes the contribution of elements on the surface over those in the underlying bulk material. However, the comparison of elements existing in the same region (surface or bulk) as described above, is reliable.

### Table 5

Elemental composition of 300 nm zeolite LTA measured by EDS.

<table>
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<tr>
<th>Atomic %</th>
<th>O</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
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<td>10.4</td>
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</table>

3.2.4. Mixed matrix composite films

To investigate the adhesion of the surface-treated LTA particles with polymers, mixed matrix films were prepared using Ultem\textsuperscript{®} as a polymeric matrix. Fig. 9 shows cross sections of membranes made with Ultem\textsuperscript{®}/untreated LTA and Ultem\textsuperscript{®}/solvothermal-LTA. Untreated LTA/Ultem\textsuperscript{®} films showed a typical "sieve-in-a-cage" morphology with voids at the interfacial regions. Furthermore – and especially for the 300 nm LTA crystals - the particles also formed clusters in the polymer matrix, resulting in a non-uniform distribution. In contrast, mixed matrix membranes fabricated with solvothermally treated LTAs were uniformly free of interfacial voids, and the individual particles were well distributed in the polymer matrix, resulting in a non-uniform distribution. Gas permeation properties of mixed matrix membranes fabricated with the two types of surfaces modified 300 nm LTAs in Ultem\textsuperscript{®} are shown in the Supporting Information (Table S1). These results show that the mixed matrix membranes containing surface-modified LTA crystals showed enhancement in both CO\(_2\) permeability and CO\(_2\)/CH\(_4\) selectivity. Based on the pre-
diction of the Maxwell model and the permeability of the polymer and the zeolite material, the mixed matrix membranes exhibited the correct trends in permeation behavior resulting from good interfacial adhesion between the surface-modified zeolite and the polymer. The mixed matrix membrane fabricated with untreated zeolite LTA exhibited poor selectivity (lower than that of pure Ultem®) due to the non-selective gas flow through the interfacial voids. However, its permeability cannot be fully explained by the Maxwell model, due to its strongly non-ideal morphology containing voids as well as aggregated particles. A more detailed investigation of the membrane permeation properties is desirable, and is the subject of future work.

4. Conclusions

Pure-silica MFI and LTA zeolite crystals were treated by solvothermal methods to deposit inorganic nanostructures on their surfaces. Our surface roughness characterizations show that solvothermal methods deposited small/fine Mg(OH)2 nanostructures on MFI surfaces, resulting in a highly roughened surface. The effect of surface treatment on the micropore volume of MFI was marginal or negligible. Zeolite/polymer adhesion was dramatically improved, leading to promising avenues for application in mixed matrix films and membranes. Solvothermal deposition of inorganic nanostructures was also successful on aluminosilicate zeolite LTA. However, concurrent ion exchange took place between Na+ ions in the LTA pores and Mg2+ ions in the reactant solution. Solvothermal treatment of LTA was tuned to deposit smaller/finer Mg(OH)2 nanostructures, resulting in a more highly roughened zeolite surface. Mixed matrix film fabrication and characterization revealed that solvothermally surface-treated LTA particles are also promising materials for the pursuit of applications in nanocomposite films and membranes.

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Appendix A. Supplementary data


References